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Demonstration and Validation of Trivalent Aluminum Pretreatment on U.S. Navy S-3 Aircraft

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Abstract:

A Trivalent Chromium Pretreatment (TCP) demonstration and validation program is currently being executed for Naval Aviation platforms. The aft section of two S-3 aircraft have being treated using a spray-on process at the Naval Aviation Depot (NADEP) at North Island, California. The coating system on these aircraft will be evaluated for corrosion performance and paint adhesion at regular intervals. The S-3s will be in service during their evaluation period. Trivalent Chromium Pretreatment demonstration and validation efforts are also underway for aircraft stationed at NADEP Cherry Point, North Carolina and NADEP Jacksonville, Florida. A thorough demonstration and validation of TCP will ensure an efficient transition to the fleet. Other opportunities are being solicited for demonstration and validation of TCP throughout the Department of Defense, the National Aeronautical and Space Administration, and original equipment manufacturers.

Background:

Aluminum pretreatment is still dominated by hexavalent chromium (chromate) processes. Environmental drivers to extensively reduce or eliminate the use of chromate conversion coatings still remain and have been recently augmented by OSHA, which plans to lower the Permissible Exposure Limit (PEL) of hexavalent chromium to 0.5 micrograms per cubic meter. The target date for compliance to this new PEL is 2001.

In addition, Executive Order 12856, Federal Compliance with Right-to-Know Laws and Pollution Prevention Requirement, sets out to ensure federal facility compliance with the pollution prevention requirements of the Pollution Prevention Act of 1990. The objectives of the Executive Order are to reduce the amount of toxic materials entering waste streams at federal facilities through source reduction and recycling, make public any toxic chemicals entering waste streams, and encourage markets for clean technologies and safe alternatives to toxic chemicals and hazardous materials.

Trivalent Chromium Pretreatment (TCP) was developed[1] to eliminate chromate waste streams and occupational exposure, directly addressing these mandates. The TCP is an ambient temperature, “drop-in” replacement for chromate conversion coatings. Additionally, the concentration of chromium in the solution is up to ten times less concentrated than standard chromate conversion coatings, reducing total chromium in wastewater.

PROBLEM

The Naval Aviation Depot at North Island, San Diego uses a solution spraying process to refinish aircraft before painting. Key steps include deoxidizing with Turco 3003 and conversion coating with Turco Accelagold. Rinse steps follow each chemical application. For environmental compliance, all wastewater is collected in a common sump and pumped into a holding tank. The metal finishing facility pays $1.10 per gallon to dispose of this waste regardless of the level of contamination with hazardous materials.

The North Island facility was selected to demonstrate the spray on application of TCP. The S-3 Viking was chosen to demonstrate the performance of TCP. The S-3 provides a unique platform with mostly aluminum alloy skin and a challenging coating system consisting of a self-priming topcoat painted directly onto the chromate pretreatment. In the TCP process, the Accelagold conversion coating was replaced by the TCP with no other changes to the original finishing process. The coating system of TCP and self-priming topcoat represents the only chromate-free finish system in the fleet. Figure 1 describes the North Island process.

DEMONSTRATION AND VALIDATION

Toxicology

A key advantage of TCP is the elimination of hexavalent chromium from the application process. A second advantage is that the pH of the TCP solution is between 3.5 and 4.0 compared to standard chromate solutions that range from 1.0 to 2.0. Eliminating hexavalent chromium solutions from spray applications will alleviate environmental, safety, and health issues including the need for expensive health monitoring due to potential exposure to chromates. It reduces the need for extensive personal protective equipment since the permissible exposure limit for trivalent chromium is 0.5 mg/m^3 (8-hour time weighted average)[2] compared to a ceiling of 0.1 mg/m^3 for chromates[3]. It also eases the handling and storage of materials since the TCP solution is not classified as corrosive.

Since the TCP solution does contain trivalent chromium and complex fluoride salts an independent toxicology analysis was performed on the solution used in the demonstration. M.B. Research Laboratories of Spinnerstown, Pennsylvania performed the following four tests using a test solution of 1.2 grams per liter chromium (III) sulfate basic and 1.6 grams per liter potassium hexafluorozirconate. Results of the tests and conclusions are described below[4].

Tests Performed:

- Single Dose Oral Toxicity in Rats/LD50 in Rats

- Acute Inhalation Toxicity in Rats/LC50 in Rats
- Primary Eye Irritation/Corrosion in Rabbits
- Primary Dermal Irritation in Rabbits

Results and Conclusions

- LD50:
  - Results: a) all animals survived the 5000 mg/kg dose in good health; b) there were no abnormal physical signs noted during any observation period; c) body weight changes were normal; and d) necropsy results were normal.
  - Conclusion: the LD50 of the test solution is greater than 5000 mg/kg.

- LC50:
  - Results: a) all animals survived the four hour 2.6 mg/l exposure; b) unkempt appearance and coating of fur with the test article were noted on the day of dosing. One instance of chromodacryorrhea was the only abnormal physical sign noted on day 1. There were no abnormal physical signs noted from day 2 through the end of the study; c) body weight changes were normal; and d) there were no abnormal necropsy observations.
  - Conclusion: the LC50 of the solution is greater than 2.6 mg/l.

- Eye Irritation:
  - Results: a) three of six eyes appeared normal at each observation period. Conjunctival irritation and discharge were noted in 3 of 6 eyes at one hour but cleared by 24 hours; and b) instances of rales, noted in one animal, were the only abnormal physical signs noted during any observation period.
  - Conclusion: the test solution is not an ocular irritant per 40 CFR 798.4500 (b) (1) & (2).

- Dermal Irritation:
  - Results: a) there was no erythema or edema noted at any observation period; and b) there were no abnormal physical signs noted during any observation period.
  - Conclusion: the test solution is not a dermal irritant per 40 CFR 798.4470 (b) (1) & (2).

Laboratory Validation

The North Island metal finishing process was simulated in the laboratory and the performance of TCP using representative substrate alloys and paint was evaluated[5]. Paint adhesion and corrosion performance were evaluated and compared to the current Accelagold and self-priming topcoat system. Table 1 details the coating systems evaluated in the laboratory. The non-chromate primer was tested to determine whether it enhances the corrosion resistance of the overall system. Since overall water volume is important to North Island, no rinse variables on the TCP were investigated to determine whether rinsing could be eliminated after applying the TCP.

Table 1: Coating Systems

Coating System	1	2	3	4	5	6	7
Pretreatment	None	TCP	CCC	TCP	CCC	TCP	TCP
Rinse	NA	Yes	Yes	Yes	Yes	No	No
Primer	85582 N	85582 N	85582 N	none	none	85582 N	None
Topcoat	SPT	SPT	SPT	SPT	SPT	SPT	SPT

Laboratory testing proved that the rinsed TCP without a supplementary non-chromate primer performed as well as Accelagold in paint adhesion with all receiving 4A or 5A ratings per ASTM 3359 (Table 2). No-rinsed versions also demonstrated acceptable paint adhesion. Coating systems with the non-chromate primer exhibited unacceptable blistering during accelerated paint adhesion tests, most likely due to interactions between the corrosion inhibiting packages of the self-priming topcoat and primer which were not designed to be used together. The test method used here is a modified version of ASTM 3359 Method A and is performed by immersing specimens in deionized water for 1, 4 or 7 days at room temperature, 120 F, and 150 F, respectively.

Table 2: ASTM 3359 Adhesion Ratings

RATING	DESCRIPTION
5A	No peeling or removal
4A	Trace peeling or removal along scribes
3A	Jagged removal along scribes up to 1/16 inch on either side of scribes
2A	Jagged removal along most of scribes up to 1/8 in on either side of scribes
1A	Removal from most of the area of the scribes under the tape
0A	Removal beyond the area of the scribes

Corrosion performance of scribed coupons exposed to 500 hours of an ASTM G-85 85 SO2 salt fog showed that the Accelagold/self-priming topcoat system performed slightly better than the TCP/self-priming topcoat system and Accelagold with the non-chromate primer and self-priming topcoat. The other paint systems showed more corrosion than the TCP/self-priming topcoat system. All systems showed excellent performance in areas away from the scribes. In general, the 7075-T6 coupons for all coating systems showed less corrosion.

Corrosion performance of scribed coupons exposed to 2000 hours of an ASTM B-117 salt fog showed that the Accelagold/primer/self-priming topcoat performed slightly better than Accelagold/self-priming topcoat system. The TCP/self-priming topcoat coupons varied in performance from as good as the Accelagold/self-priming topcoat coupons to slightly worse, showing additional corrosion at the scribes. The remaining paint systems showed more corrosion than the TCP/self-priming topcoat system, with the presence of blisters on many 2024-T3coupons. In general, the 7075-T6 coupons for all coating systems showed less corrosion.

Depot Demonstration and Validation

The demonstration and validation of spray on TCP at the depots is based on a two-step approach. First, demonstrate the process and material on representative parts or small sections of an air vehicle. Second, with acceptable performance in step one, demonstrate on a full airframe. In this project, the aft section of the S-3 was treated as step one. The aft section contains representative alloys on the full S-3 skin and offers all variations of application angles. The remainder of the aircraft serves as a control.

The TCP solution was prepared as separate concentrates of chromium (III) sulfate basic and potassium hexafluorozirconate. The final mixture and dilution with deionized water was made an hour before application on the aircraft, yielding a solution of approximately 1.2 grams per liter chromium (III) sulfate basic and 1.6 grams per liter potassium hexafluorozirconate. Solution mixing and application procedures were developed in coordination with Arcova; a private company developing a commercial product based on the solution used in this demonstration.

North Island paint shop artisans applied the TCP[6]. Shop tools normally used to apply chromate conversion coating were used. Photo 1 shows the barrel from which the solutions are sprayed and the pump apparatus.

Photo 1: NADEP North Island Spray Apparatus

Photo 2 shows the application of TCP on the tail of the aircraft. The TCC solution has a low viscosity relative to conventional conversion coating materials (e.g. Turco 3003TWA & Accelagold). Given that few surfaces on an aircraft's moldline are horizontal, thin liquids run directly off many of the surfaces. A thickener may be beneficial to the process if a minimum dwell time of the TCP in contact with the aluminum is recommended for developing suitable coatings. The surfaces of the tail were kept wet with TCP solution for 10 to 20 minutes.

As seen in Photo 3, the front portion of the aircraft was treated with the chromate conversion coating material, yielding a gold surface finish. The TCP was then applied over the horizontal and vertical tail surfaces, and aft fuselage. Fuselage Station 496 (just behind the flaps and forward of the vertical tail, Photo 2) is the approximate transition area of the two conversion coating materials. The overspray of the TCP on the Accelagold was determined by laboratory testing to not have any detrimental effect. Visual observance during the application process confirmed the laboratory results. Standard application procedures were followed, whereby, the conversion coating materials were sprayed on wetted surfaces beginning at the bottom and then working upward. A second application pass was made with the TCP based on process guidance from Arcova.

Photo 2: Application of TCP

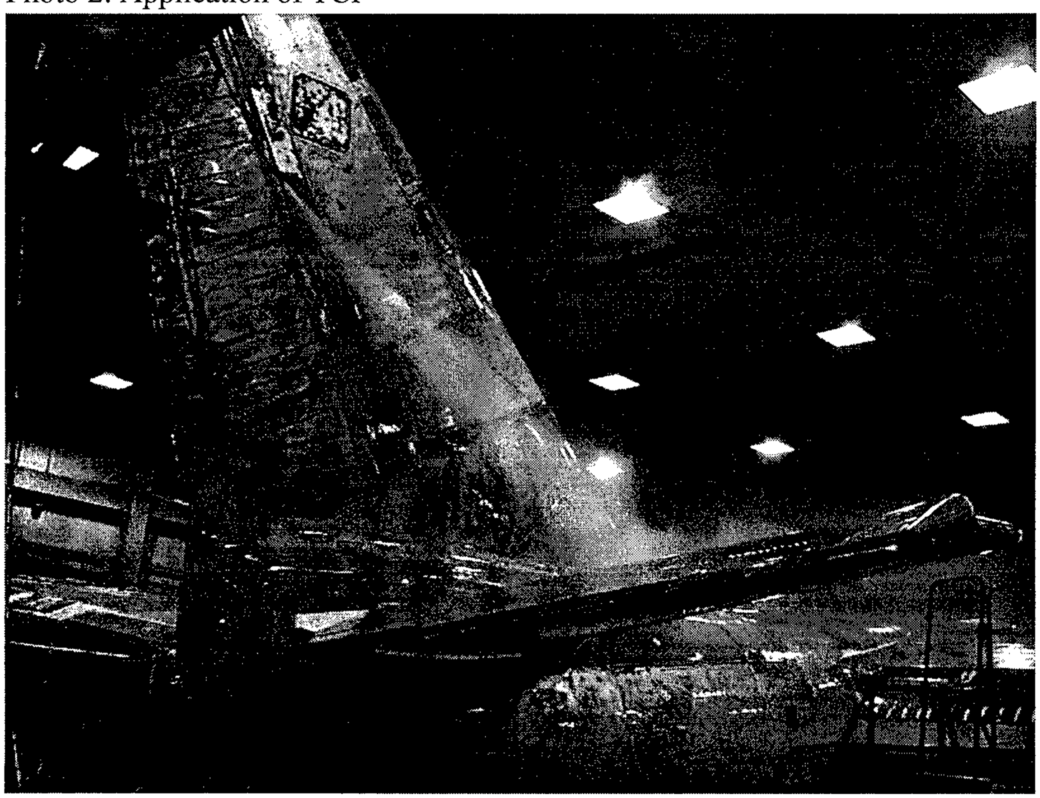


Photo 3: S-3 After Application of Accelagold

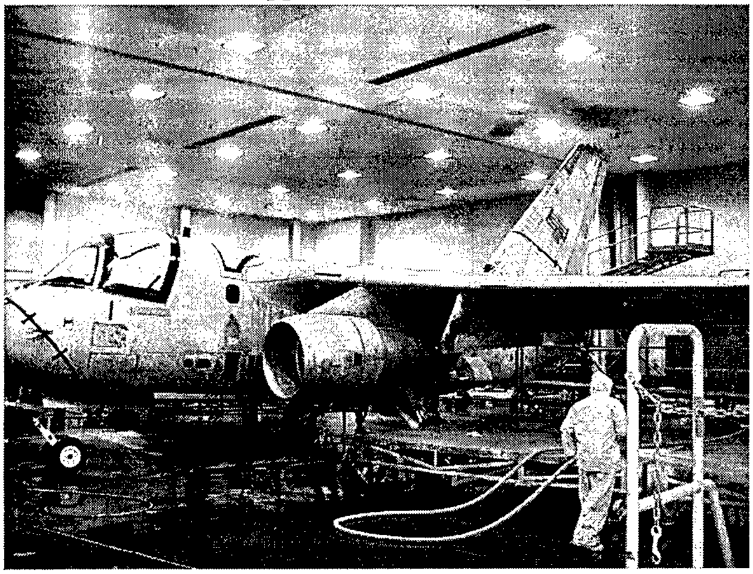
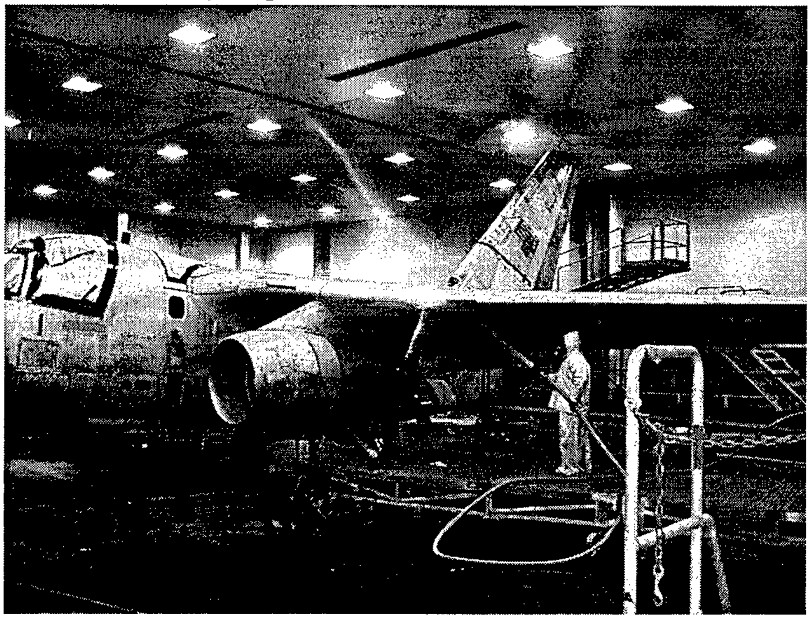


Photo 4 depicts the aft section minutes after the application of TCP. The lack of color in the applied film was noted by the artisans and makes it difficult for them to visually verify film formation during solution application.

Photo 4: Fuselage Station 496- pretreatment transition area

Photo 5 depicts the post operation rinsing procedure. The total time required for the standard rinsing step is from 10 to 20 minutes using two hoses. Rinse hoses are 2" diameter with city water pressure between 50-70 psi. Process improvement in rinsing includes minimizing or eliminating total rinse volume. For this demonstration, the concern over the issue of corrosion in fayed areas caused from solution entrapment, or the residue left by puddles of solution, precluded the use of a no-rinse process.

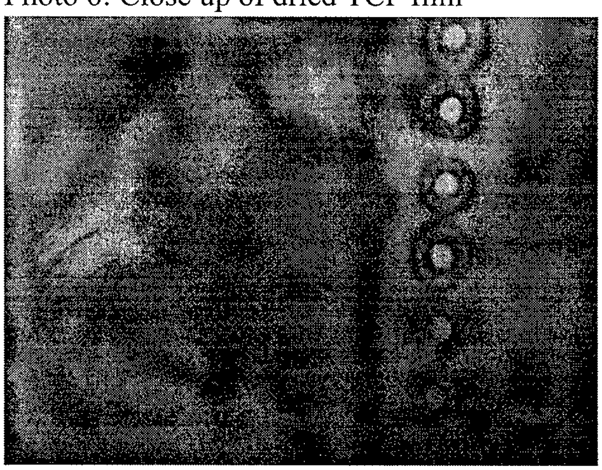
Photo 5: Rinsing Step



A close-up of a TCP-treated area prior to paint is depicted in Photo 6. Upon close inspection a bluish tint is evident. Many of the areas with anodize appeared unaffected by the TCP, as it would be with Accelagold.

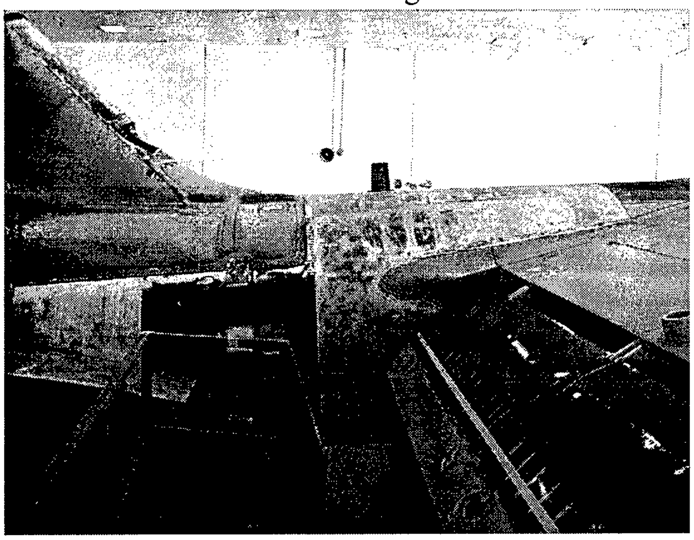
Measurements of surface conductivity were taken six hours after the conversion coating was applied. Electrical resistance on the order of kilo-Ohms was measured indicating a (non-conductive) film was present.

Photo 6: Close up of dried TCP film



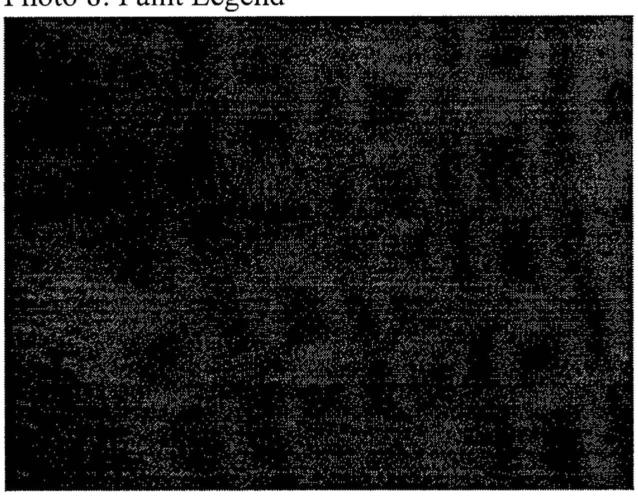
A reasonable depiction of the transition area between Accelagold and TCP (i.e., FS 496) treatments is shown in Photo 7. The golden color of the panel above the wing is a splendid example of chromate treated aluminum alloy. The multitude of colors in the aft sections are: paint (green; Type II primer, and gray topcoat), yellow 'borders' on gray painted panels (fiberglass), and TCP on the door and areas above it.

Photo 7: Post conversion-coating treatment of FS 496



It is significant to note that the moldline finish system of the aircraft's tail is chromate free. Self-priming topcoat (TT-P-2756) is used without primer. Photo 8 is the paint legend stenciled on this aircraft.

Photo 8: Paint Legend



Photos 9 and 10 show the fully painted S-3 BUNO 160144. This aircraft was painted on July 25, 1999 and is attached to VS-31, Jacksonville, FL. Photo 9 provides a close up of the aft section with TCP. The aircraft 'sell date' from North Island was July 31, 1999.

Photo 9

Photo 10

The second application of TCP was to an S-3A SDLM aircraft at North Island August 2, 1999. The application process is consistent with that of the first S-3A sprayed with TCP eleven days earlier.

Plans

The two S-3s will be evaluated at six and 12 months for TCP performance compared to the remainder of the aircraft. Paint adhesion and substrate corrosion will be critical criteria. With successful performance on the aft sections, at least one full S-3 aircraft will be treated with TCP and evaluated over an extended period. No rinse versions of the North Island spray process will also be investigated over the next 12 months.

Concurrent efforts are underway at NADEP Cherry Point and Jacksonville. Initial focus will be on wipe-on type application procedures similar to existing procedures at the depots. Air platforms at these facilities will be selected based on coating systems, performance envelope, and availability.

Acknowledgements

Thanks to the NAVAIR Aviation Pollution Prevention Program (W2210) for support of this effort.

References

[1] Pearlstein, F., and Agarwala, V.S., U.S. Patent 5,304,257, "Trivalent Chromium Conversion Coatings for Aluminum," April 19, 1994.
[2] OSHA Table Z-1; Standards- 29 CFR 1910.1000 Table Z-1, "Limits for Air Contaminants."
[3] OSHA Table Z-2; Standards- 29 CFR 1910.1000 Table Z-2.
[4] Appendix- Toxicology Report, M.B. Research Laboratories, Spinnerstown, PA, MB Project #98-7031, December 1998.
[5] Matzdorf, C., Kane, M.J., and Green, J.L., "Laboratory and Field Testing of Trivalent Chromium Aluminum Pretreatment," presented at the 1999 DOD/Industry Aerospace Coatings Conference, May 18, 1999.
[6] "Cleaning and Surface Preparation for Elastomeric, Polyurethane Primer, TT-P-2760," LPS NI 136 Revision B, January 20, 1994.